

An Investigation of Sodamide and of Its
Reaction-products with Phosphorus
and with Phosphorus Penta-
chloride.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

—BY—

WILLIAM PHILLIPS WINTER

1904

EASTON, PA. :
THE CHEMICAL PUBLISHING COMPANY.
1904.

An Investigation of Sodamide and of Its
Reaction-products with Phosphorus
and with Phosphorus Penta-
chloride.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

—BY—

WILLIAM PHILLIPS WINTER

1904



EASTON, PA. :
THE CHEMICAL PUBLISHING COMPANY.
1904.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41552322_0101

CONTENTS.

I. Sodamide :

Historical	5
Preparation.....	7
Properties	7
Examination of gases insoluble in NaOH formed by decomposition with water.....	9
Table of gasometric analyses	12
Interpretation of results	13
Effect of low temperature and of use of nitrogen.....	14
Theoretical consideration of source of nitrogen.....	16
Examination of color change in sodamide.....	17
Detection of nitrous acid.....	18
Detection of hyponitrous acid.....	19
Detection of nitrogen and of nitric oxide.....	19
Conclusions on twofold source of nitrogen.....	21
Cyanamide reaction.....	22
Analysis of disilver cyanamide	22

II. Sodamide and phosphorus pentachloride :

Historical	24
Experimental.....	24
Separation and purification of sublimate.....	26
Properties of the insoluble portion	27
Methods of analysis.....	27
Table of analyses	28
Interpretation of results.....	29

III. Sodamide and yellow phosphorus :

Preliminary experiments.....	30
Preparation of the material.....	30
Properties	32
Historical	32
Analysis :	
Volumetric for phosphine and hydrogen	34
Table of volumetric analyses.....	35
Volumetric determination of ammonia	36
Gravimetric determination of sodium and phosphorus.....	37
Reactions and composition.....	38
Simultaneous recognition of hypophosphorous, phosphorous and phosphoric acids.....	40
Ammonium molybdate reduction by phosphine.....	41
Quantitative determination of sodium phosphide.....	41
Synthetic determination of nature of initial reaction.....	41
Theoretical consideration of source of hydrogen	42
Significance of ammonia-nitrogen in the material.....	43

Sodamide as a reagent.....	44
Summary	45
Biography	46

ACKNOWLEDGMENT.

Acknowledgment is gratefully made by the writer to the valued instruction which he has received in the lecture-room and laboratory from Professors Remsen, Morse, and Jones.

This investigation was suggested by Professor Renouf and carried out under his guidance. To him the writer desires to express gratitude for his coöperation and helpful counsel.

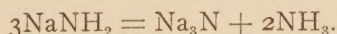
The advice of Professor Morse has been frequently sought and it has proved most helpful. From Dr. Gilpin and Professor R. W. Wood assistance has likewise been received, which is hereby acknowledged.

An Investigation of Sodamide and of Its Reaction-Products with Phosphorus and with Phosphorus Pentachloride.

THE history of the preparation of sodamide dates from 1809, when Sir Humphry Davy,¹ in England, and Gay-Lussac and Thénard,² in France, almost simultaneously discovered the amides of sodium and of potassium. They were carrying on investigations to determine the composition of ammonia and they led a strong current of the latter gas, for several hours, over the pure metal heated in a glass retort to about 300°. The glass of the retort was considerably etched, and the semicrystalline mass of sodamide obtained was olive-green in color.

They investigated and sought to analyze it. Davy plunged pieces of sodamide under the mouths of jars filled with water, transferred the unabsorbed gas to a eudiometer and determined that hydrogen was formed in the decomposition of sodamide by water. Gay-Lussac and Thénard, by strongly heating the substance, obtained two-fifths of the ammonia that had disappeared in the reaction; at a higher temperature nitrogen and hydrogen gases were formed in the ratio of 2.5 of the former to 1 of the latter in quantities to account for one-fifth more of the ammonia. Decomposition of the residue by water yielded the remaining portions of ammonia.

These investigators are also responsible for a method, published by them, for the preparation of sodium nitride. They stated that when sodamide is strongly heated it decomposes in accordance with the equation



They described the nitride as a dark brown powder. Titherly,³ in 1894, carefully repeated these experiments, employing a pure quality of sodamide, and he found that strong heat completely dissociates it. He concluded that the so-called nitride was to be

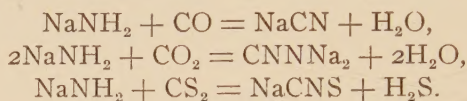
¹ *Phil. Trans.*, **1**, 39 (1809).

² *Recherches Physico-chimiques*, **1**, 337-356.

³ *J. Chem. Soc. (London)*, **65**, 504, and **71**, 460.

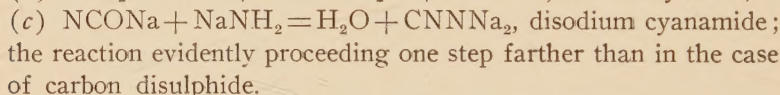
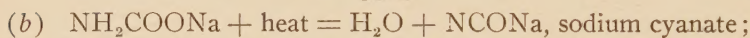
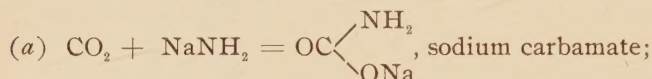
ascribed to impurities in the sodium employed and to contamination by the constituents of the glass of the retorts.

Beilstein and Geuther,¹ in 1858, prepared sodamide in the same way as the discoverers did. They analyzed it by determining the amounts of sodium and of ammonium chlorides formed when it was decomposed by hydrochloric acid, and they further investigated its reaction products when currents of dry carbon monoxide, carbon dioxide and carbon disulphide were led over the heated sodamide. The reactions are,

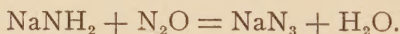


The presence of water produced secondary reactions with sodamide not included in the equations.

Drechsel² showed that the reaction with carbon dioxide was not analogous with the one given for carbon disulphide and he proved that the nature of the reaction with carbon dioxide was better expressed in consecutive stages, thus:



Wislicenus³ heated sodamide in a stream of dry nitrous oxide. It affords a simple and effective means for the synthesis of sodium triazoate,



This method has been recently considerably improved by Dennis and Browne.⁴

Titherly⁵ carried on an extensive investigation of sodamide. He made the discovery that it can be made in vessels of pure metal, such as silver or iron, in considerable quantity and free

¹ *Ann. Chem.* (Liebig), **108**, 88.

² *J. prakt. Chem.* (2), **11**, 308; and **16**, 203.

³ *Ber. d. chem. Ges.*, **25**, 2084.

⁴ *J. Am. Chem. Soc.*, **26**, 577.

⁵ *Loc. cit.*

from the contaminations that glass always imparts to it. Sodamide thus made is of a pure white color. Titherly employed two different synthetical methods for the analysis of his product, the results of which confirmed each other and pointed conclusively to the hitherto accepted formula for sodamide. He further showed that disodimide and sodium nitride could not be formed by continued substitution of ammonia hydrogen by sodium, but that certain organic residues have the power to substitute one or both of the hydrogen atoms of sodamide.

PREPARATION OF SODAMIDE.

The preparation of sodamide presents no especial difficulties. Fig. 1 represents the apparatus as used. *A* is a flask in which concentrated ammonia water is heated with a low flame. *B* is an empty gas-washing bottle, kept cool to condense excess of moisture. 1, 2, 3 and 4 are drying towers, filled with soda-lime. *C* is a tube filled with pieces of sodium. It may conveniently be about 40 cm. long. *D* is a wrought iron retort, made in two parts, which fit together at the flange in the center. It is capable of holding about 200 grams of sodium when filled nearly to the flange. Before heating the sodium, ammonia is passed for a long time through the apparatus, and at the conclusion of the experiment the sodamide is allowed to cool in the current of ammonia. Precautions are taken to have a *continuous* supply of ammonia.

The writer has found, by careful tests, that a silver-plated crucible is rapidly attacked, but that a pure wrought iron crucible can be used repeatedly, the sodamide formed in it showing no trace of iron when its solution in water was acidified and treated with potassium ferrocyanide. The crucible was heated for about five hours with a single Bunsen burner, so regulated as to prevent the distillation of the sodamide into the air. More elaborate apparatus has been described for the preparation of sodamide, but the chief merit of the apparatus here described is that it can be quickly put together from apparatus to be found in almost any laboratory and with it sodamide of excellent quality has been repeatedly made.

PROPERTIES.

Omitting the discussion of the better known properties of sodamide, we have noted that under certain circumstances, not fully

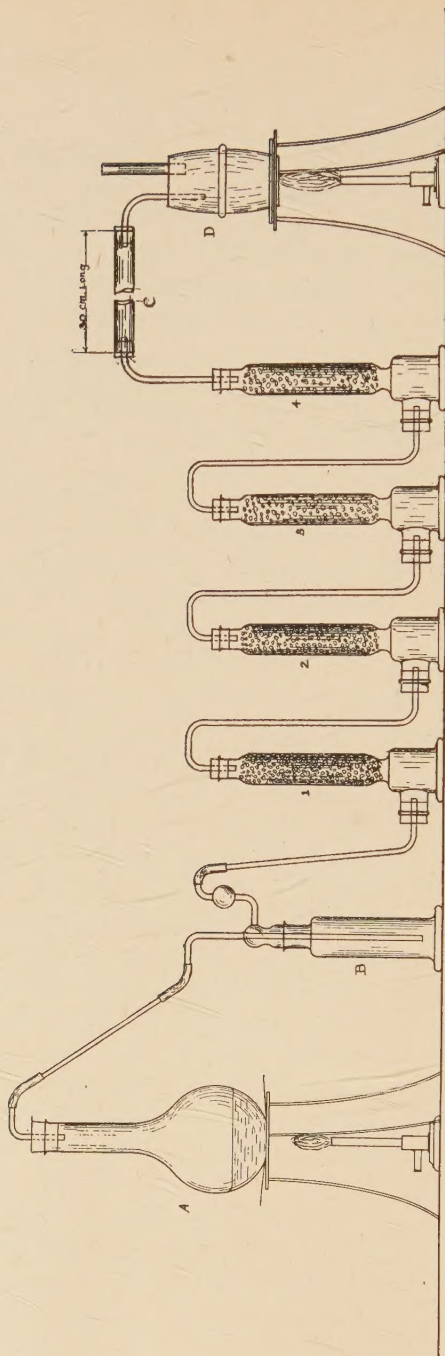


Fig. 1.

understood as yet, sodamide kept in dry, glass-stoppered bottles slowly undergoes a peculiar color change from white to yellowish brown. The change is more rapid if the sodamide is powdered. Light or its absence was not responsible for the change. It does not necessarily depend on the method of its manufacture for samples of the same sodamide were powdered and kept side by side in different vessels for some weeks. The change had taken place in part of the samples only. The change is, in some way, dependent on the amount of dry air which comes in contact with the sodamide and upon the duration of exposure to it, for it was observed that: (1) The sodamide which had been kept longest had undergone the greatest change when conditions otherwise were the same; (2) small bottles, with *accurately fitting* stoppers, not opened repeatedly, as many of the samples were, underwent little or no change in their contents; (3) the powdering of sodamide brings the air more completely into contact with the sodamide.

When sodamide is thrown into water the behavior is quite similar to that of sodium, forming a globule which floats about on the water and at last explodes. The globule formed by sodamide that has undergone the color change often changes to a brown or black color and explodes with increased violence. If the water is warm, these phenomena are more noticeable. It was the peculiar sharp explosion that first suggested the possibility of the presence of traces of a triazoate or some such compound as a working hypothesis.

Sodamide is rapidly decomposed by absolute alcohol with evolution of ammonia and formation of sodium ethylate. The alcohol is heated to boiling, if the sodamide is added rapidly, but since it does not float on the alcohol there is no final explosion. While the white sodamide imparts no color to the alcohol until after long standing, the yellow variety colors it a deep brown, out of all proportion to the color in the sodamide used. With the yellow variety there is usually formed also an insoluble residue.

EXAMINATION OF THE INSOLUBLE GASES FORMED ON DECOMPOSING SODAMIDE WITH WATER.

It has long been known that water breaks down sodamide into sodium hydroxide, setting free ammonia; and Davy also

noted the formation of hydrogen. In all the sodamide examined by the writer there was found also traces of nitrogen, the ratio between hydrogen and nitrogen depending not only on the way in which the sodamide was prepared, but also on the length of time and manner in which it was kept previous to analysis. The apparatus in which these experiments were carried on is represented in Figs. 2 and 3. Carbon dioxide, dried by sulphuric acid, was first conducted through the apparatus (Fig. 3),

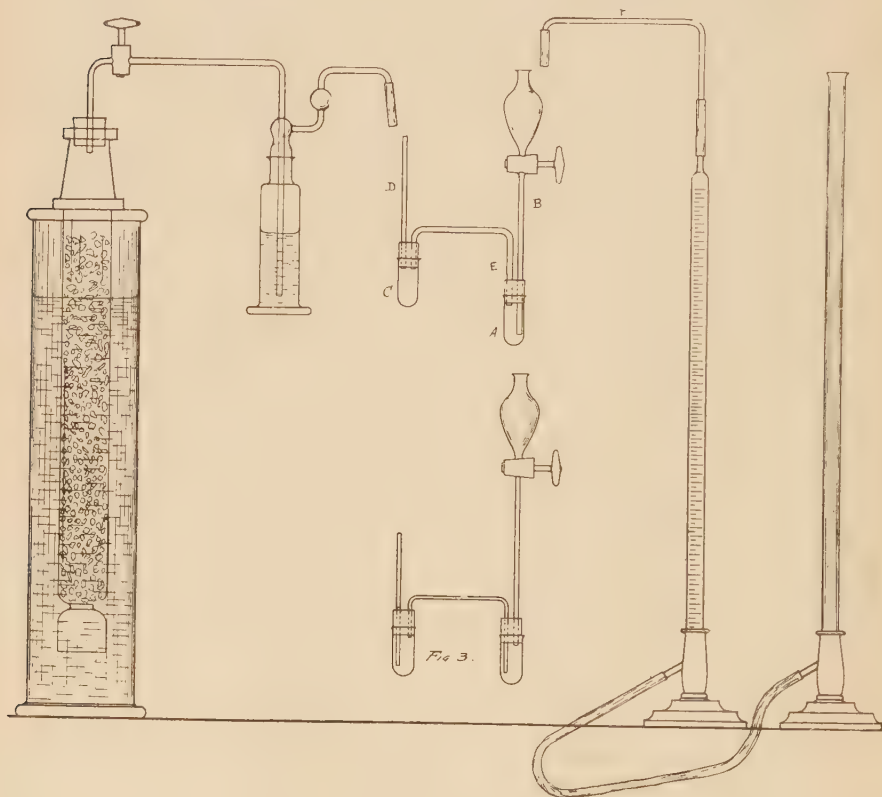


Fig. 2.

the gas entering at *D* and escaping at *B*. The weighed substance (finely powdered) was then introduced into *A* and the current of carbon dioxide continued until the gas, issuing from *B*, was *completely* absorbed by a strong solution of caustic soda. Without removal of the stoppers the tubes were shifted into the position

shown in Fig. 2, the stop-cock of *B* closed and the funnel filled with distilled water. The tube *D* was connected to the capillary of a Hempel's burette, *F*, completely filled with a 10 per cent. solution of caustic soda. In some experiments it was found necessary to introduce into the burette measured portions of pure oxygen. Water was slowly dropped from the funnel into the sodamide, diminished pressure being produced in the burette. At the end, water was admitted to drive over every trace of gas, and the carbon dioxide and ammonia were completely absorbed.

Hydrogen was determined by explosion in a eudiometer, the nitrogen being estimated by difference. The identity of nitrogen was established beyond question by sparking known volumes of it in the presence of excess of oxygen and traces of caustic potash for several hours with a high voltage current. By absorption with phosphorus the remaining gas was shown to consist solely of the excess of oxygen introduced.

In the analyses given, Sodamide I was made by heating 175 grams of sodium for four hours with the full flame of a Bunsen burner. At the end of the operation the crystallized sodamide which, in all cases, was of a white color, was broken away from some unchanged sodium. Sodamide II was made from 60 grams of sodium heated three and one-half hours. There was no apparent excess of sodium. Sodamide III was made from 110 grams of sodium heated strongly for three hours; no excess of sodium. Sodamide IV was made from 42 grams of sodium heated one and one-fourth hours. The excess of sodium was separated from the sodamide as described above. Sodamide V was made by heating 50 grams of sodium four hours. There was no excess of sodium. All the samples were at once transferred to well-stoppered glass bottles and kept in the dark.

For the analysis small portions were taken from different parts of the material, finely ground, and placed in glass-stoppered weighing-tubes in calcium chloride desiccators. The decomposition was effected by water in the apparatus described. The latter had been previously tested by allowing it to stand fourteen hours under the diminished pressure produced by the difference in level of the two communicating arms of the Hempel's burette amounting to about 4 feet. No change of level was noted, thus indicating that

there was no entrance of air by leakage into the apparatus during the experiment. The reaction with the first drop or two of water is extremely violent. Sixty to eighty cc. of gases are formed and driven over into the burette within the first few seconds, and the generator becomes very hot. Since most of the gases are ammonia and carbon dioxide the absorption is so rapid that, notwithstanding the diminished pressure, the liquid is sometimes drawn back into the generator with resultant explosion of the latter from confined gases. The partial combination that takes place between some of the ammonia and the carbon dioxide is also responsible for the rapid back-suction.

TABLE OF VOLUMETRIC GAS DETERMINATIONS OF DIFFERENT SAMPLES OF SODAMIDE.

Sodamide I.			
Weight in grams.	Total cc. of gases.	Percentage of nitrogen.	Remarks.
0.5957	17.25	16.09	
1.4143	37.65	19.28	
0.2537	9.8	32.37	
0.8410	22.9	38.93	
0.7073	18.3	38.42	
0.6966	17.0	41.85	
0.8464	21.4	44.43	
0.6589	20.9	63.58	} After standing six weeks.
0.4772	13.8	63.62	
0.4073	13.7	65.81	
Sodamide II.			
1.1229	4.4		
1.3489	3.6		
1.1349	4.6	95.05	
Sodamide III.			
0.8513	5.0	72.58	
0.9819	6.34	75.84	
0.7777	4.3	85.18	
0.6937	4.6	89.14	After standing twelve weeks.
0.9195	6.65	92.00	After standing fourteen weeks.
Sodamide IV.			
0.6250	18.78	6.15	} Freshly analyzed.
0.7525	23.0	5.22	
Sodamide V.			
0.6221	1.2	49.16	} Freshly analyzed.
0.6654	1.2	51.66	
0.4122	1.8	...	After five weeks <i>no</i> color change. Trace of hydrogen. The portion kept five weeks (<i>with</i> resultant change of color) exploded under analysis.

INTERPRETATION OF RESULTS.

Sodamide III was not analyzed until some weeks after its preparation. Frequent explosions of the generator (Fig. 2) and other difficulties in the application of the method with the apparatus at hand hampered, to some extent, the work. But it was not sought by this method to set forth an exact analysis of sodamide, for the apparatus with which to do the work was that which would appertain to a "proximate" and not to an "exact" series of gas determinations. The purpose was to seek a possible explanation for the presence of free nitrogen among the decomposition products of sodamide, and to the facts deduced from the analyses bearing on this phase of the problem we now turn.

(1) Sodamide is not a stable substance; it changes its composition not only from frequent opening, but apparently under certain conditions on long standing in closed vessels.

(2) It is only apparently homogeneous; sodium hydroxide and free sodium in minute particles are always present, and evidence seems to be conclusive that a number of sodium compounds, to which reference will be presently made, are to be found in traces in it.

(3) Sodamides I and IV were made to contain excess of sodium. The free metal could be separated quite readily since the sodamide is white, brittle and crystalline, while the sodium is dark, waxy, massive and floats upon the top of the sodamide which has been formed. Nevertheless the analyses of these, when contrasted with the other samples, show a relatively large gas evolution and (naturally) a low nitrogen percentage because of the hydrogen present. The only other gas found in the products of decomposition of sodamide by water, besides ammonia, was hydrogen and the percentage of this gas can, therefore, be simply deduced from the percentages of nitrogen. The explanation for the liberation of this hydrogen is that minute particles of sodium become encrusted with sodamide in the retort and escape the action of the excess of ammonia. Accordingly, the proper preparation of sodamide requires a *prolonged* heating in a slow current of ammonia.

(4) When sodamide is thus made, the total gas insoluble in sodium hydroxide solution falls to a minimum, but is never zero,

and, at the same time, the percentage of nitrogen rises nearly to 100 per cent.

(5) Another striking fact to be observed in the analyses is that invariably the percentage of nitrogen rose rapidly when the compound is kept for some time. Reference to this will be made again later.

(6) There is an actual diminution in the amount of hydrogen found among the decomposition products of sodamide that has stood for some time, and in many cases an actual and not merely a relative increase in the amount of nitrogen. The former is to be accounted for as follows: The minute particles of sodium are slowly acted upon at the ordinary temperature by the atmosphere of ammonia always to be found over sodamide, and thereby new sodamide is formed. But while the hydrogen evolved thus falls to a minimum the total amount of gas formed does not fall in like proportion. On the contrary, it more often increases. This points to a subtle change going on simultaneously with the disappearance of the sodium whereby a compound capable of yielding nitrogen is being continually formed. This hypothetical compound is never absent in any sodamide we have made or examined. An average of three determinations of gases, insoluble in water, yielded by a freshly prepared sodamide made to contain a minimum of free sodium, gave 4.5 cc. of gases per gram of sodamide. The same sample four weeks later gave as an average of three determinations 5.9 cc. of gases per gram, and the volumetric percentage of nitrogen was increased, while that of hydrogen had decreased. This relation is also well illustrated in the results given in the table (page 12).

EFFECT OF LOW TEMPERATURE AND OF USE OF NITROGEN.

It has been already mentioned that Beilstein and Geuther¹ had noted the formation of cyanamide, CNNH_2 , when sodamide is heated with dry carbon dioxide. Since the latter gas was used to displace air in the apparatus in which the sodamide was decomposed, and since the considerable heat of the reaction might have formed small quantities of cyanamide whose subsequent decomposition might account, in some unexplained way, for the presence

¹ *Loc. cit.*

of nitrogen, the experiments were repeated with some other gas to see whether any change would occur in the amount or the character of the gases developed. Oxygen suggested itself as a gas which could easily be absorbed by alkaline pyrogallol solution, but attempts to use it resulted in explosions. Nitrogen was then used and to determine the increase of gas the apparatus was calibrated in terms of the graduation of the Hempel's burette.

0.5901 gram of sodamide yielded, when decomposed by water in the presence of nitrogen, 46.25 cc. of gases. Deducting 41.45 cc. for the capacity of the apparatus, there remained 4.8 cc. as the amount of gases attributable to the decomposition.

0.6937 gram of the same sodamide decomposed a few days previously in the presence of carbon dioxide yielded 4.6 cc. of gas. It was evident from this that carbon dioxide did not exert any appreciable influence on the amount of gas evolved by the decomposition of sodamide with water. Examination of the solution left in the generator showed only a trace of sodium cyanamide as a by-product of the reaction, and it is not at all clear how its presence in considerable amount could have affected the percentage of nitrogen.

In the second place it was assumed that if heat had anything to do with the evolution of nitrogen from sodamide in its decomposition, the amount could be diminished by working near the zero temperature. Accordingly, the generator (A, Fig. 2) was immersed in ice-water and the funnel filled with the same.

0.5747 gram decomposed under these conditions yielded 4.3 cc. of gases. This is quite comparable with the yield at ordinary temperatures.

The conclusion is then unavoidable that neither temperature nor the nature of the diluent gas exerts any appreciable effect on the amount of gas generated, and the presence of free nitrogen constantly among the products of decomposition of sodamide by water can only be ascribed to the presence of a compound of the triazooate order whose instability can account for the phenomena as observed.¹

¹ The invariable presence of nitrogen in the decomposition of sodamide by water is not to be referred to a constant error of some sort in the conduct of the experiment, for this same method was repeatedly used in the analysis of a substance made from sodamide which yielded on decomposition by water chiefly hydrogen and phosphine. In the greater number of instances no nitrogen could be detected in the gas evolved. To this work, reference is more fully made in the latter part of this paper.

THEORETICAL CONSIDERATIONS OF SOURCE OF NITROGEN.

Three theories have been advanced to account for this nitrogen.

(1) That the considerable heat suddenly developed by dropping water on sodamide dissociates some ammonia into its elements. This is highly improbable for, if it were the case, the hydrogen formed should bear a simple ratio to the nitrogen, or, at any rate, should be in excess. Inspection of the analyses show that in many cases only traces of hydrogen are present.

(2) That minute quantities of disodimide or of sodium nitride break down, yielding nitrogen. This is equally untenable, for not only has their formation in this manner been shown to be highly improbable, but, even if present, such compounds being ammonia derivatives would yield ammonia on treatment with water.

(3) That traces of sodium or ammonium triazoate, NaN_3 or NH_4N_3 , would yield nitrogen on decomposition through the sudden heat development by the addition of the first drop or two of water. There is no evidence that this class of salts decompose quietly, though some of them explode on sudden heating.¹ It was noted that the material in the generator, usually about 500 mg., was spattered about violently by the first contact with water and there is unquestionably a very sudden rise in the temperature of the mass.

To account for the presence in sodamide of these bodies capable of yielding nitrogen and its oxides, recourse must be had to the well-known slow oxidation which ammonia can undergo; thus,



The first product is unknown, the second is hyponitrous acid. If oxidation stops at this stage, the unstable hyponitrous acid breaks down into nitrous oxide and water, and the formation of nascent nitrous oxide lends some probability to the suggested explanation that a compound is formed by it with sodamide analogous to, if not identical with, sodium triazoate. It can not be denied that a reaction which proceeds rapidly at a definite elevated temperature may also proceed with greatly reduced velocity at ordinary temperatures.

The presence of traces of oxygen is not unlikely in ammonia

¹ *Ber. d. chem. Ges.*, **24**, 3346; *J. prakt. Chem.* (2), **58**, 278 and 307.

generated from strong aqueous solution and passed through large drying towers of soda-lime. Moreover, the short exit tube of the retort in which the sodamide is made and the central flange of the body of the retort permit slight access of air to the mass within. Very little sodium triazoate is demanded to account for the nitrogen formed. Sodamide yielding 5.5 cc. of nitrogen per gram would require less than 1 per cent. of sodium triazoate. To account for the increase of nitrogen obtained by decomposing sodamide which has been kept in stoppered bottles for some time, it must be further assumed that the oxygen of the air, the ammonia, and the traces of sodium can slowly react at ordinary temperatures.

EXAMINATION OF COLOR-CHANGE IN SODAMIDE.

In the attempt to isolate this compound, experiments were undertaken which led into a qualitative study of the changes which sodamide undergoes on keeping. A number of interesting facts were ascertained and, furthermore, a line of investigation was indicated which it was impossible for the writer, in the limited time at his disposal, to fully exploit.¹ The phenomena which led to this part of the work are here recapitulated and, after a brief description of the work done, some theoretical conclusions are appended which await further confirmation.

- (1) The color change in sodamide on keeping.
- (2) The violence (often explosive) of the decomposition of sodamide by water.
- (3) The examination of the solution obtained through this decomposition.
- (4) The twofold source of nitrogen in the breaking-down of the colored variety of sodamide by water.
- (5) The reaction with alcohol.
- (6) The cyanamide reaction.

The color change is evidently the key to the explanation of some of the other phenomena. The facts are these: Sodamide, when freshly made, is white, solid and crystalline. Upon long

¹ The work is not described in this paper in the order in which it was carried on. The reactions of sodamide with phosphorus pentachloride and with yellow phosphorus were first taken up, and as much of the time as was left was devoted to the study of sodamide itself.

keeping it becomes, with few exceptions, yellowish-brown, somewhat porous, and it loses its crystalline appearance. That this was not due to change induced by atmospheric moisture and consequent breaking down into sodium hydroxide colored by iron, was assured by analysis of one specimen of sodamide which had undergone the color change. It was shown that deterioration had only partially taken place, for the ammonia found, calculated as NH_3 , gave 35.85 per cent. and 35.61 per cent. as the result of two determinations, whereas the theoretical amount is 41.07 per cent. The negative result of the test for iron has already been given. The effect of this color-change upon the sodamide is very evident. Two samples of the same material were powdered and so treated that air had more complete access to one than to the other. At the end of five weeks the one tightly closed had suffered no change in color, could be decomposed in the usual way in the apparatus shown in Fig. 2, and showed the usual diminution in hydrogen with but a slight increase in nitrogen. The other portion was dark in color and exploded with violence, when the first drop of water was admitted upon it from the funnel, in three successive repetitions of the experiment. When thrown into water it decomposed energetically with flame. Thrown into alcohol it left a considerable white residue. In all cases the decomposition of colored sodamide seems more energetic than that of the white variety, and the explosion of the globule which floats upon the surface of the water is more violent.

When the two varieties of sodamide are dissolved in alcohol the yellow variety imparts a deep brown shade to the liquid and this is only partially discharged by acids. White sodamide imparts no color. An insoluble residue is left after the solution of the yellow variety. Decomposition of this by acids yields, as one of the products, carbon dioxide, thus pointing to the existence of traces of sodium carbonate. It is in this residue that sodium triazotate should be found, if found at all, since sodium triazotate is almost insoluble in absolute alcohol.

DETECTION OF NITROUS ACID.

The examination of the solution formed by throwing sodamide into water also gave distinctive reactions, differentiating the yellow

and the white varieties. Without exception the yellow sodamide solution responded to the various tests for nitrous acid, yielding fumes of nitrogen peroxide with excess of dilute sulphuric acid, and giving a deep brown coloration with *m*-phenylenediamine. The solution of the white variety failed to yield these tests.

In the theory already elucidated to explain the possible presence of a compound of the triazoate order, it is evidently only necessary to carry the oxidation of the ammonia one step farther to account for the presence of nitrous acid. The formation of nitrous acid after the sodamide has been kept for a considerable time and not during the process of its manufacture seems conclusive evidence that either the nitrogen of the air can enter into reaction with sodamide without the aid of heat, or, more probably, that the oxygen of the air can effect oxidation of the nascent ammonia formed by the slow breaking-down of a part of the sodamide. This oxidation product would then combine with the base to form sodium nitrite; but since the latter is undoubtedly present it is not at all unlikely that traces of sodium hyponitrite are also present, for its formation would involve merely the supposition of the presence of one of the intermediate products of oxidation. The presence of hyponitrous acid, as we have seen, renders possible the presence of sodium triazoate.

DETECTION OF HYPONITROUS ACID.

Hyponitrous acid, according to Hantzsch,¹ exists in two stereoisomeric varieties, one of which, called isohyponitrous acid, yields no yellow precipitate with silver nitrate, but it gives a white precipitate with mercuric nitrate; the normal hyponitrous acid, on the contrary, yields yellow silver hyponitrite and no precipitate with mercuric nitrate. In applying this test there was obtained a slight precipitate with mercuric nitrate pointing to the existence of one of the above hyponitrous acids.

DETECTION OF NITROGEN AND OF NITRIC OXIDE.

When the alkaline solution obtained by decomposing yellow sodamide with water was acidified with dilute sulphuric acid in a small vessel from which the air had been displaced by carbon dioxide, a number of gases were evolved. The apparatus was

¹ *Ann. Chem.* (Liebig), **299**, 67; *Ber. d. chem. Ges.*, **30**, 2356.

connected with a Hempel's burette in order to collect and examine the gases. Dilute sulphuric acid was admitted slowly through a dropping funnel, and at first there was a considerable evolution of carbon dioxide. This, together with any ammonia which may have been disengaged before neutralization of the strongly alkaline liquid, was completely absorbed by shaking with the solution of sodium hydroxide in the burette. After the neutralization of the alkali an excess of acid was introduced and the solution was boiled. The gases were completely driven into the burette and, after shaking, there remained a considerable residue unabsorbed. By admitting this into a eudiometer partially filled with oxygen over water there was noted the formation of nitrogen peroxide and consequent diminution of volume through its absorption; but a residue still remained which did not combine with oxygen even on passing the spark. Into another portion of the gas pure hydrogen was passed and the mixture was sparked, but there was no evidence of any combination having occurred. Hence it was highly improbable that either oxygen or nitrous oxide was present in any appreciable amount in the gases and conclusion seemed unavoidable that the remaining gas was nitrogen. A third portion was passed into a Bunsen gas pipette filled with aqueous solution of ferrous sulphate. The formation of the characteristic brown compound of nitric oxide with ferrous sulphate occurred and a residue of nitrogen remained. The nitric oxide was in slight excess, as will be seen from the following results obtained by the decomposition of three separate portions of sodamide, the lack of homogeneity in which has been shown elsewhere as well as in this series.

TABLE OF RATIOS OF NITROGEN TO NITRIC OXIDE.

First Portion—in eudiometer with oxygen.

- (1) 1 part nitrogen to 2.5 parts nitric oxide
- (2) 1 part nitrogen to 2.58 parts nitric oxide*

Second portion—determined as above.

- (1) 1 part nitrogen to 1.5 parts nitric oxide
- (2) 1 part nitrogen to 1.4 parts nitric oxide

Third Portion. Nitric oxide absorbed by ferrous sulphate.

- (1) 1 part nitrogen to 1.21 parts nitric oxide
- (2) 1 part nitrogen to 1.3 parts nitric oxide

While the decomposition of nitrous acid can account readily for the presence of nitric oxide and nitrogen peroxide, it fails completely to account for the presence of nitrogen. Hyponitrous acid usually breaks down into nitrous oxide and water, but when violently decomposed, water, nitrogen, and oxygen are produced. If both acids are present, secondary reactions between nitric oxide and oxygen would explain the absence of oxygen, and excess of nitric oxide would remain if nitrous acid were present in greater amount than hyponitrous acid, as is the case.

The possibility that exists here for the formation and presence of other compounds in minute traces is evident from a consideration of such work as the following: Von Brackel¹ has obtained hydrazine from the reduction of hyponitrous acid. Hantzsch² has converted nitroso hydroxylamine into hyponitrous acid and has shown the possibility not only of stereoisomers of this acid, but also a structural isomer, nitramide, NO_2NH_2 . Divers,³ van der Plaats,⁴ and Paal⁵ have each done work showing the intimate relationship that exists between nitrites, hyponitrites, hydroxylamine, hydrazine, etc., and in many cases there are conflicting statements.

CONCLUSIONS ON TWOFOLD SOURCE OF NITROGEN.

The study of the decomposition of sodamide by water has revealed some interesting facts concerning the nitrogen evolved:

(1) All sodamide, white or yellow, yields nitrogen when decomposed by water in an atmosphere of carbon dioxide. This nitrogen is evolved in the presence of an excess of alkali.

(2) Yellow sodamide in the above reaction when further treated with excess of acids yields a second portion of nitrogen, and nitric oxide is also evolved.

(3) The solution formed by decomposing white sodamide with water does not yield, with excess of acids, any gases which are not absorbed by the sodium hydroxide.

The significance of these facts is that a compound, at least

¹ *Ber. d. chem. Ges.*, **33**, 2115.

² *Loc. cit.*

³ *Proc. Roy. Soc.*, **19**, 425.

⁴ *Ber. d. chem. Ges.*, **10**, 1507.

⁵ *Ibid.*, **26**, 1026.

analogous to a triazoate, is broken down in alkaline solution and completely decomposed by acids. A salt of nitrous or hyponitrous acids is indifferent to alkaline reagents, but is decomposed by acids.

It will be necessary to prepare sodamide under the most varied possible conditions, to expose it to long contact with quantities of dry air, both at ordinary and at somewhat elevated temperatures, and to verify by preparation in quantity of hyponitrous acids and its related compounds a series of reliable tests which may be employed in investigation of the yellow variety of sodamide. This work is not unimportant if sodamide is to be used as a reagent, because of the complicated side reactions which such traces may render possible.

SODIUM CYANAMIDE FROM SODAMIDE.

Beilstein and Geuther¹ have already shown that when dry carbon dioxide is passed in a slow stream over heated sodamide sodium cyanamide, CNNa_2 , is formed. In the course of certain experiments by the writer it was noted that when a cylinder containing a small amount of water, heated almost to boiling, was connected to the carbon dioxide generator, so that there might be a continued supply of the gas, a shower of brilliant sparks occurred when sodamide, finely powdered, was sifted into the cylinder. The reaction was most complete when the temperature of the water was between 60° and 100° , and when the gas in the cylinder was not too much diluted with hydrogen, nitrogen or air.

Examination of the water solution at the end of the experiment showed the presence of cyanamide, the most satisfactory yield being found in those experiments in which there had been the greatest production of sparks. A quantitative analysis was made of the silver cyanamide produced by addition of ammoniacal silver nitrate solution to a solution of cyanamide or any of its salts. After drying the amorphous, brilliant yellow silver cyanamide at 130° for a sufficient time, the analysis was carried on as follows:

(1) For silver, gravimetrically as silver chloride. 0.3576 gram gave 0.3930 gram AgCl , equivalent to 0.2958 gram Ag , or 82.71 per cent. The theory calls for 84.34 per cent.

¹ *Loc. cit.*

Beilstein and Geuther obtained $\left\{ \begin{array}{l} 81.34 \text{ per cent.} \\ 81.68 \text{ per cent.} \end{array} \right.$

Drechsel obtained $\left\{ \begin{array}{l} 80.6 \text{ per cent.} \\ 81.6 \text{ per cent.} \end{array} \right.$

Mulder obtained 82.9 per cent.

It was pointed out by Mulder that the explanation for these uniformly low results was probably to be found in the presence of silver dicyandiamide, $\text{C}_2\text{N}_4\text{H}_3\text{Ag}$, in small quantity, formed through the tendency to polymerize, so frequently displayed by cyanogen compounds.

(2) For nitrogen, volumetrically by Dumas' method, giving 11.37 per cent.; calculated, 10.97 per cent.

(3) For carbon and hydrogen by combustion with copper oxide in presence of a copper spiral, which gave, C, 5.47; H, 0.35; calculated, C, 4.68 per cent.

These results for nitrogen and carbon serve to confirm the presence of a polymer of cyanamide for, while a portion of the water obtained may not unlikely be attributed to traces of moisture absorbed by the apparatus and reagents or imperfectly removed from the oxygen, it is hardly probable that both nitrogen and carbon should be in excess of the theoretical, while at the same time silver was deficient, unless traces of a compound were present containing a higher proportion of carbon and of nitrogen and a lower one of silver, as silver dicyandiamide does.

SODAMIDE AND PHOSPHORUS PENTACHLORIDE.

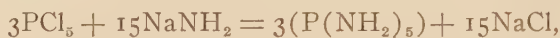
HISTORICAL.

A number of weeks after the investigation, herein described, had been commenced, Stock and Hoffman¹ published an account of the preparation of a new nitride of phosphorus, P_3N_5 , by treating phosphorus pentasulphide with liquid ammonia and heating the complex compound formed. It may also be formed by heating the pentasulphide directly in a stream of ammonia gas to 230° .

It seemed not improbable that sodamide, acting on phosphorus pentachloride, could effect a transformation such as



or



or some similar compound of phosphorus with amidogen or its residue.

The work of Joannis,² who obtained boron triamide by passing the vapor of boron trichloride together with hydrogen through liquid ammonia; of Hugot,³ who worked with sodammonium, $NaNH_2$, on phosphorus and on arsenic; of Besson,⁴ who obtained as a final product phospham, PN_2H , from the double salt obtained by treating phosphorus pentachloride with ammonia; and of others who have used liquid ammonia and ammonia gas, in experiments of a similar character points clearly to the fact that compounds containing ammonia-nitrogen have been made in considerable variety and are of unusual chemical interest.

PREPARATION.

When powdered sodamide and phosphorus pentachloride are brought together in *small quantities* in a dry test-tube and the mixture slightly warmed a violent reaction ensues, accompanied by flame and by the evolution of a white extremely light powder, the greater part of which settles on the sides of the tube.

¹ *Ber. d. chem. Ges.*, **36**, 314.

² *Compt. Rend.*, **135**, 1106.

³ *Ibid.*, **121**, 206; **126**, 1719; **127**, 553.

⁴ *Compt. Rend.*, **114**, 1264.

The bottom of the tube is usually melted out by the heat generated. The white powder, which had sublimed on the walls of the tube, was collected and thrown into water. The greater part of it dissolved readily, and this was found by qualitative tests to consist of ammonium chloride, sodium chloride, and traces of phosphorus compounds. A small portion was found to be insoluble in water.

The results attained in this rough qualitative way seemed to warrant more careful experiment, and accordingly the following apparatus was devised for the work: A large bell-jar of about 20 cm. diameter and 30 cm. in height was fitted to a ground glass plate from which had been cut a portion of sufficient width to admit the glass tube through which pure nitrogen was admitted. The nitrogen, made from molecular equivalent amounts of sodium nitrite and ammonium chloride, was stored in a gasometer, washed through three drying bottles containing strong sulphuric acid and passed over heated copper gauze to remove traces of oxygen and of oxides of nitrogen. Fitted tightly into the neck of the bell-jar was a wide glass tube, which could be raised or lowered at will. To the top of the tube was attached a funnel which served to direct the fall of the materials to be introduced into the small porcelain dish placed within the jar. A slow stream of nitrogen was conducted into the apparatus for a considerable time, the tube in the neck of the bell-jar having been drawn up its full length to facilitate the expulsion of air from the apparatus. Without interrupting the flow of gas, small, nearly equal, portions of powdered sodamide and of phosphorus pentachloride were alternately dropped through the funnel tube, which had been partially lowered. The reaction usually took place at once, but if not, a warmed glass rod, inserted through the tube, was sufficient to start the reaction. The energy of the reaction in the atmosphere of nitrogen is much less than in the air, and if care is exercised in the successive addition of the two reacting materials, very little of the white product was projected into the air. Sufficient heat was generated by the union of the first portions to carry the operation on to the end. The time consumed in introducing into the apparatus about 36 grams of phosphorus pentachloride and 30 grams of sodamide was about two hours.

The addition of either reagent in excess soon interrupted ignition of the mixture, but action is at once restored with considerable vigor when change to the other reagent is made. The apparatus was allowed to cool in the stream of nitrogen and upon opening the bell-jar its sides and the bottom plate were found to be covered to a considerable depth with a deposit of a white, light powder in a state of extremely fine subdivision. In the porcelain dish was a solid core consisting largely of sodium chloride and of traces of the reagents used.

SEPARATION AND PURIFICATION OF THE SUBLIMATE.

To separate the soluble from the insoluble portions was found to be an exceedingly difficult task. When the powder is thrown into water, much of it goes into solution, a small portion settles, but the water assumes and retains a milky appearance, which does not disappear after two months' standing. It has been found impossible to separate and purify the residue in this way. The pores of the paper or of the asbestos-filter quickly become clogged and the portion of the residue which comes into contact with the filter forms a gummy mass and adheres to it with such tenacity that separation of filter and precipitate is impossible after drying. The yield of insoluble powder is so small that washing by decantation results in almost complete loss of the precipitate. Washing with alcohol or other organic solvents is impracticable, owing to the quite general insolubility of the chlorides which it is desired to remove. If the powder be treated with moderately dilute hot nitric acid, an insoluble residue soon settles and the supernatant liquid becomes clear. Specimens of the powder for analysis were obtained in this way. Brown fumes of nitrogen peroxide were evolved on heating and these were ascribed at first to the action of the hydrochloric acid formed from traces of phosphorus oxychloride, which are undoubtedly present. The results of analysis indicate that it is far more likely that the oxidation takes place in the insoluble compound itself.

Acetic acid of 25 per cent. strength can also be used to separate the soluble impurities—the powder obtained being somewhat more voluminous. If hydrochloric acid is used, there is also rapid settling of the insoluble residue, but when this is dried at 100° in an

air-bath it is semi-liquid and gummy, and on further heating to 145° the mass becomes, after cooling, gray, hard, tenacious, and vitreous.

The above acids, if diluted further, as well as sulphuric acid or solutions of the fixed alkali hydroxides would not effect separation of the two portions. After decantation from the acid washings the powder was dried in glass vessels at 100° and separated from the glass by the aid of a piece of stiff platinum wire. The yield was about 2.5 per cent. of the weight of sublimate used.

The separation of the insoluble portion was also attempted by heating the white powder in a combustion tube in a slow stream of pure dry nitrogen. The details of this method have not been fully worked out, but it was noted that at a dull red heat a white vapor distilled away and was carried through a strong solution of potassium hydroxide without apparent absorption or change. It seems likely that a method of fractional sublimation can be devised which will separate the white powder into three portions, *viz.*:

(1) An easily volatile mixture of phosphorus and ammonium chlorides.

(2) The insoluble portion desired.

(3) A non-volatile residue of sodium chloride.

PROPERTIES OF THE INSOLUBLE PORTION.

The powder obtained by treatment with nitric acid was a white, nearly tasteless, odorless compound, exceedingly inert. Boiling with the strong mineral acids did not affect it and similar treatment with aqua regia or with concentrated potassium hydroxide solution affected it, if at all, to so slight an extent as to be unnoticeable, if the action was not prolonged.

METHODS OF ANALYSIS.

Three methods were devised which were effective in decomposing it:

(a) Heated with water in a sealed tube for three hours to 180° it was decomposed and the solution, on opening the tube, yielded the odor of ammonia and responded to the molybdate of ammonia test for phosphoric acid.

(b) Treated with an aqueous solution of hydrofluoric acid and

a little sulphuric acid in a platinum crucible, the compound was broken down upon the application of gentle heat. A solution of the residue gave the test for phosphoric acid.

(c) Heated to dull redness for four hours in a combustion tube with a mixture of powdered hydroxide and nitrate of potassium, ammonia was evolved and a phosphate remained behind. A silver boat was used and a slow stream of dry air was forced over the heated mass.

The above methods were all employed in the analysis of the compound. In the practical application of the first method it was noted that when water alone was used the tube was badly attacked and several grams of silica were separated. It was found best to employ dilute hydrochloric or sulphuric acid for the twofold purpose of diminishing the separation of silica and of fixing the ammonia in the non-volatile condition. In all determinations of phosphoric acid by this method, however, it was necessary to separate silica in the usual way before estimating the phosphorus as magnesium pyrophosphate. The second method was available for the determination of phosphoric acid only. It possessed the advantage of rendering unnecessary the previous removal of silica. The third method was not free from silica contamination, since it was impossible to prevent distillation of the contents of the silver boat on to the combustion tube.

In the first method the ammonium salt was decomposed by distillation with sodium hydroxide, the ammonia being absorbed by a standard acid, while in the third method the ammonia was received directly into the acid.

TABLE OF ANALYSES OF THE INSOLUBLE RESIDUE.

Powder purified by nitric acid.			
Weight. Gram.	Per cent. of P.	Per cent. of N.	Method of decomposition.
0.0864	33.67	19.42	Fusion with KOH and KNO_3 4 hours.
0.0739	40.31	20.58	" " " " " 5 ½ hours.
0.0810		21.54	" " " " " 5 ½ hours.
0.0578	40.31		By hydrofluoric acid.
0.0638	40.26	20.75	Sealed tube with HCl at 180° .
0.1108		21.50	" " " " " 180° .
Vitreous mass obtained by hydrochloric acid.			
0.0630	26.56	15.11	In sealed tube, 180° .
0.1008	27.58	14.57	" " " " 180° .

Analysis of portion dissolved out by nitric acid.

Weight of material.	Weight of NH_4 .	Weight of Cl.	Weight of P.	Weight of Na.
3.608	0.2879	1.6998	0.2512	0.7382

Corresponding to :

	Grams.
NaCl	1.8735
NH_4Cl	0.8524
H_3PO_4	0.7944
Undetermined	0.0777
	3.608

INTERPRETATION OF RESULTS.

Whatever the composition of the compound represented by the above analyses may prove to be, it is clear that the phosphorus and the nitrogen stand in the ratio of 1:1. The results of the analysis of the compound, purified by hydrochloric acid, show that it was, to a considerable extent, broken down and they are, therefore, not considered. The analyses correspond to the formula PO_2N or to some polymer of it. Such a formula requires 40.24 per cent. phosphorus, 41.53 per cent. oxygen, 18.22 per cent. nitrogen. There was found 40.28 per cent. phosphorus, 20.35 per cent. nitrogen. The excess of nitrogen is not surprising when the method of preparation of the material for analysis is considered.

The phosphamic acid described by Schiff,¹ the identity of which was called in question by Gladstone and Holmes,² agrees quite well in analysis and in all properties save one, that of its solubility in water, with the compound we have obtained. A series of metaphosphimic acids, PONHOH , empirically isomeric with Schiff's compound has been described by Stokes³ and he has suggested that in this instance there may possibly occur a complex polymer of metaphosphimic acid, $(\text{PONHOH})_x$. But since nitric acid undoubtedly oxidizes the original product of the reaction and since water probably hydrolyzes it, the analysis, as given, throws little light on the original product of the energetic reaction between phosphorus pentachloride and sodamide.

¹ *Ann. Chem.* (Liebig), **103**, 168.² *J. Chem. Soc.* (London), **17**, 226.³ *Am. Chem. J.*, **15**, 198, and **18**, 630.

SODAMIDE AND PHOSPHORUS.

PRELIMINARY EXPERIMENTS.

When sodamide in fine powder and yellow phosphorus in small pieces were heated together under boiling benzene (boiling-point 79°) there was no action beyond a partial solution of the phosphorus. The experiment was repeated with xylene (boiling-point 137°) with no evidence of combination having taken place. The same results followed the use of aniline (boiling-point 183°), although the aniline was attacked by the reagents with the formation of complex organic products. Finally, heavy lubricating (paraffin) oil was employed (boiling-point 214° or more) with no better results. But when the two substances were brought together in a test-tube, combination took place with great energy on slight warming of the tube. An incrustation of red phosphorus was formed on the tube, the bottom of which was usually melted out in the reaction. Particles of an almost black substance, formed by the reaction, produced when thrown into water, a spontaneously inflammable gas and emitted a most pronounced disagreeable odor. Red phosphorus and sodamide heated together rather more strongly produced a similar compound.

PREPARATION OF THE MATERIAL.

Attempts were then made to prepare the compound in test-tubes, flasks, etc., properly supplied with a stream of pure, dry nitrogen. However, the heat evolved by the reaction always shattered the glass and prevented the preparation of any considerable amount. Porcelain vessels could be used without fear of breakage and the experiment whereby about 12 grams could be prepared at once was carried out as follows: The bottom of a wide-mouthed bottle of about 3 liters capacity was covered with glass beads to a sufficient depth to hold in place a large porcelain crucible about 30×30 mm. The bottom of the crucible was kept from direct contact with the bottom of the bottle that the latter might not be cracked by local heating. Through the neck of the bottle was passed a gas delivery tube, reaching to the bottom of the bottle, and a wide glass tube, about 30 mm. in diameter, which could be

raised before beginning the experiment to assist in driving out air, but lowered almost to the mouth of the crucible when the reagents are to be dropped in. A gas tube was passed into this wide tube and connected by a Y with the same nitrogen apparatus described in the reaction with sodamide and phosphorus pentachloride. By means of pinch-cocks nitrogen could be delivered into the bottom of the bottle, into the vicinity of the reacting substances, or simultaneously through both tubes at will. The stream of nitrogen was not discontinued at the end of the experiment until the apparatus was quite cool. The reaction proceeded with far less vigor in an atmosphere of nitrogen than in air. The heat of a warmed glass rod was sufficient to start the reaction. Precautions had to be employed to prevent too great a rise in temperature, for with such rise much of the phosphorus was converted into the red modification. It has not been found possible to prevent entirely this formation of red phosphorus, but under favorable conditions not much in excess of 1 per cent. of the compound consists of it.

When the air had been displaced, the finely powdered sodamide and the phosphorus in small pieces were dropped through the long tube into the crucible in small successive portions. The phosphorus was dried as thoroughly as possible by absorbent paper or, better, by benzene. The material could not be removed from the atmosphere of nitrogen before it had become cool nor subjected to any friction without danger of spontaneously inflaming. It was, therefore, moistened with carbon disulphide when cool, removed to a mortar, pulverized under the same liquid and freed from excess of phosphorus by repeated washing in carbon disulphide, which had been redistilled and then dried over calcium chloride.

The attempt was made to remove any excess of sodamide which it might contain by washing with absolute alcohol, but it was found that the entire compound was broken down with evolution of phosphine. In fact, even the treatment with carbon disulphide was observed to set free appreciable amounts of ammonia and of phosphine, and this was taken as a significant indication of the presence of certain unstable components of the reaction. The purified powder was dried at the ordinary tem-

perature in an atmosphere of nitrogen, transferred to tightly stoppered containers and placed in a phosphorus pentoxide desiccator.

PROPERTIES.

The chocolate-red powder thus obtained is sensitive to traces of moisture and gives off continually a disagreeable odor suggestive of garlic. In the air it rapidly deliquesces and becomes lighter in color. When heated in air it gives off ammonia and phosphine, while the sodium salts of hypophosphorous and phosphorous acids remain. Heated in a supply of dry carbon dioxide gas it gives off the two gases above and there remain sodium carbonate, hypophosphite and phosphite. Water, dilute acids and alcohol break it down in the same way, but if alcohol is used, the phosphine is not inflammable. Hydrogen is also evolved in considerable quantity by decomposition with water or acids. Absolute ether, chloroform or benzene are without apparent action on the compound.

HISTORICAL.

Before entering upon the analysis or constitution of this compound brief reference must be made to work which has been done along similar lines. Gay-Lussac and Thénard, and also Davy supposed that phosphides of the alkali metals could be formed by heating the elements together in nitrogen.

In 1829, Magnus¹ devised a method for the preparation of potassium phosphide, K_3P , which was later used by Vigier² in preparing the similar sodium phosphide for use in an organic research. Phosphorus was melted under petroleum (boiling-point 120°) and bits of potassium were added from time to time. The oil was distilled off, the excess of phosphorus removed by carbon disulphide and the residue dried at a low temperature in a current of dry carbon dioxide. He stated that the compound separated carbon as well as phosphine when treated with water or dilute acids, and that he was not able to get the phosphide in a state of purity. Vigier's sodium phosphide was described as a black compound. He made no attempt to analyze it. In the course of this work his experiments

¹ *Pogg. Ann.*, **17**, 527.

² *Chem. News*, 1861, p. 273.

were repeated, resulting in the verification of his method and description, and, in addition, a partial analysis was made. Magnus gives nothing but the formula for his potassium phosphide, making no statement as to any analyses upon which he based his conclusions. Rose¹ caused potassium and phosphorus to combine in a flask in the presence of hydrogen. At the end of the experiment the excess of phosphorus was distilled off. He obtained a crystalline mass of the color of "japanned copper."

Bunsen² showed that sodium phosphide was formed by heating sodium and sodium phosphate together in a tube and he recommended this as a qualitative test for the presence of phosphorus.

The phosphides of calcium, tin, zinc, copper, magnesium, iron, and aluminum have been made,³ and their composition and properties established. The phosphides of the heavy metals, as would be supposed, are much more stable than those of the alkalis.

Sodammonium, NaNH_3 , and potassammonium, KNH_3 , have, in the hands of Hugot and Joannis, working independently, been of considerable importance. These two reagents are made by the action of liquid ammonia on sodium or on potassium. They decompose slowly at ordinary temperatures,⁴ and a little more rapidly in the light than in the dark, forming sodamide or potassamide and hydrogen. Sodammonium in excess, red phosphorus and sodium, left in contact for several days, formed $\text{P}_2\text{H}_3\text{Na}_3$, ($\text{Na}_3\text{P.PH}_3$), sodamide and ammonia. The phosphide is described as a yellow crystalline body yielding phosphine in the presence of moisture.⁵ The authors claim that if the red phosphorus is in excess, $\text{P}_3\text{K}.3\text{NH}_3$ is formed, which loses its ammonia at 180° . It is always more or less contaminated with potassamide. With sodium, $\text{P}_3\text{Na}.3\text{NH}_3$ is formed, which becomes P_3Na at 180° .⁶ If no sodium or potassium is used, or if phosphine be led into sodammonium or potassammonium, the substituted phosphines NaPH_2 and KPH_2 are formed.⁷

¹ *Pogg. Ann.*, **12**, 547.

² *Ann. Chem.* (Liebig), **138**, 292.

³ *Centrbl.*, **2**, 642 (1890); *Bull. Soc. Chim.* (3), **27**, 568; "The Electric Furnace," by Moissan-Lenher, p. 291.

⁴ *Compt. Rend.*, **112**, 392.

⁵ *Compt. Rend.*, **126**, 1719, and **127**, 553.

⁶ *Ibid.*, **121**, 206.

⁷ *Ibid.*, **119**, 557.

The chemistry of the phosphides of hydrogen is also closely interwoven with this work, because the phosphine produced in the decomposition of the compound by water was relied upon as a measure of the amount of sodium phosphide in it. It was Thénard¹ and, later, Gatterman,² who first separated and determined the constitution and properties of gaseous, liquid and solid phosphines. The former also noted the presence of free hydrogen in phosphine as ordinarily made.

Hoffman³ showed that in all the common methods of producing phosphine the gas was diluted with from 6 to 80 per cent. of hydrogen (volumetric). When phosphine was made in the ordinary way, by heating an aqueous solution of potassium hydroxide with yellow phosphorus, only from 10 to 40 per cent. of the gas obtained was phosphine. Alcoholic potash gave about 45 per cent. phosphine under similar circumstances. If calcium phosphide was used, the yield of phosphine was better, but the phosphine was far from pure. The amount of hydrogen was very changeable and was not accounted for. Even the decomposition by heat of pure phosphoric acid yielded a phosphine which contained at least 6 per cent. of hydrogen. The decomposition of pure phosphonium iodide, PH_4I , is the only method of obtaining pure phosphine. He also showed that fuming nitric acid, as well as the vapor of chlorine and of bromine, render non-inflammable phosphine self-inflammable.

Bodroux⁴ pointed out that temperature has something to do with the amount of hydrogen produced; in the case, at least, of the decomposition of certain phosphides. When aluminum or magnesium phosphides are decomposed with water they yield phosphine slowly. If the water be above 50° or if acids are used, much hydrogen is developed; if ice-water is used, no hydrogen is formed.

ANALYSIS. VOLUMETRIC GAS DETERMINATION.

The powdered compound was decomposed by water or by acids in the apparatus described for the examination of sodamide (see Figs. 2 and 3) in an exactly similar way. The

¹ *Ann. Chem.* (Liebig), **55**, 27.

² *Ber. d. chem. Ges.*, **23**, 1174.

³ *Ibid.*, **4**, 200.

⁴ *Bull. Soc. Chim.* (3), **27**, 568.

atmosphere of carbon dioxide prevented the phosphine from inflaming, although the reaction was violent and a great amount of heat was liberated. The solution remaining in the generator *A* was strongly alkaline, responded to the tests for hypophosphorous acid and contained a small amount of red phosphorus. The volume of the gases remaining in the burette after the absorption of the ammonia and the carbon dioxide was noted and they were then passed into a Bunsen gas pipette filled with a freshly prepared solution of cuprous chloride in concentrated hydrochloric acid to absorb the phosphine. Measured portions of the unabsorbed gas remaining were then transferred to a eudiometer and exploded over mercury with electrolytic oxygen. Nitrogen, when it occurred, was determined by difference.

Portions made at different times showed a variation in composition, and analyses of the same material at widely different periods further showed deterioration to be continuous. In the preparation of the first portion sodamide was used in excess, which was known to yield considerable nitrogen when decomposed by water. In the other two portions excess of phosphorus was used. Only a few representative data are given:

TABLE OF VOLUMETRIC GAS-ANALYSES OF THE PRODUCT OF THE PHOSPHORUS-SODAMIDE REACTION.

Portion I.—Excess of Sodamide I.				
Weight in grams.	Total gases in cc. not absorbed by NaOH.	PH ₃ . Per cent.	H. Per cent.	N. Per cent.
0.8664	23.73	47.01	45.77	7.22
0.3690	11.25	47.70		
0.9612	31.15	47.35	45.85	6.80
1.1212	34.45	47.17	46.74	6.09
0.4446	15.05	46.84		
0.7050	24.40	46.70		
1.1614	35.95	46.87	46.04	7.00
0.6109	19.55	46.80	44.44	8.76
1.9516	65.45	45.76		
0.7667	26.15	45.00		
Portion II. Sodamide III.—Phosphorus in excess.				
0.9043	69.05	28.06	71.80	0.00
0.8095	67.95	24.65	75.15	
0.7800	62.35	24.13	75.67	0.00
0.6764	59.95	19.63	80.00	0.00
0.8748	79.25	19.44	80.20	
0.6752	61.60	18.90	81.00	
Portion III. Sodamide III.—Phosphorus in excess.				
0.4126	57.00	16.10	83.80	
0.4190	63.80	15.00	84.20	0.00
0.8069	57.85	14.65	85.00	0.00
0.4765	67.30	14.80	85.00	

These determinations were made through considerable intervals and with minor variations of method to demonstrate the tendency of the compound to deteriorate. Why there should occur so wide a variation in the yield of phosphine and hydrogen in the case of Portion I as contrasted with the other two portions remains unexplained.

Although Bodroux¹ had shown temperature to be a controlling factor in the amount of hydrogen obtained from aluminum and magnesium phosphides, it was found in similar experiments with the sodium phosphide, made by the method of Vigier, that only a slight change could be detected.

0.2987 gram, decomposed by water at 20°, yielded 39.01 per cent. phosphine, the remaining percentage being hydrogen.

0.3467 gram, decomposed by water at 0°, the generator being immersed in ice-water, yielded 40.48 per cent. phosphine. It will be remembered that Bodroux obtained no hydrogen when he used ice-water.

Ammonia was determined by two methods:

(1) A weighed portion of the compound was placed in a small weighing bottle and lowered into a pressure bottle containing some six-normal hydrochloric acid. The top was adjusted and the apparatus was set away for twenty-four hours for the vapor of the acid to slowly attack the compound. At the end of that time substance and acid could be intimately mingled without development of dangerous pressures. The contents of the bottle were then distilled with excess of sodium hydroxide into a standard acid and the liberated ammonia determined in the usual way by means of titration.

0.2418 gram of the compound gave 22.49 per cent. of ammonia.

(2) A second weighed portion was placed in a small U-tube and hydrochloric acid gas was forced or drawn over it and then through two U-tubes containing dilute sulphuric acid. The dilute acid itself was finally brought into contact with the substance by rapidly boiling the hydrochloric acid. The contents of the three U-tubes were then proceeded with as above.

0.4434 gram of the compound gave 22.8 per cent. of ammonia.

¹ *Loc. cit.*

GRAVIMETRIC DETERMINATION OF SODIUM.

Sodium was determined gravimetrically as sulphate. The phosphorus was removed by oxidation with nitric acid, precipitation by lead acetate and lead carbonate, and after filtration from the phosphates, excess of lead was removed by hydrogen sulphide.

0.4627 gram of compound gave 0.6313 gram of sulphate, equal to 44.22 per cent. Na.

0.1559 gram of compound gave 0.2098 gram of sulphate, equal to 43.63 per cent. Na.

DETERMINATION OF PHOSPHORUS.

In the determination of phosphorus the pressure bottle method was employed. At first the attempt was made after introducing the small tube containing the material into the bottle in which was some dilute nitric acid, to bring the substances immediately into contact. For this purpose a long pair of tongs was used to grasp and tilt the bottle. But such sudden pressure was developed that the bottle was broken into small pieces by the force of the explosion. In subsequent experiments the small tube of material was allowed to stand in an upright position within the bottle for a long time. Fuming nitric acid was placed in the bottle because it was certain that its vapors would more surely oxidize volatile phosphorus compounds and complete the oxidation to phosphoric acid of lower oxygen compounds of phosphorus. The action within the pressure bottle was usually violent. In from one to two hours after closing the bottle an explosion with flame usually occurred of sufficient force to shatter the weighing-glass which contained the substance. Owing to the fact that small weights of material were used, that the pressure bottle had a capacity of 500 cc., and that in the first one or two hours much of the ammonia had been "fixed," the bottle withstood the force of the shock. After the lapse of several hours the pressure bottle was gently heated in a water-bath without removal of the stopper. The bottle was then opened and its contents were evaporated on the water-bath almost to dryness. The phosphorus was determined as magnesium pyrophosphate. The determination was verified by first precipitating a second portion to be analyzed with ammonium molybdate and then with magnesium mixture.

In a third determination, to show that there was no conversion of the phosphates into metaphosphate, the solution was boiled with a large excess of water for thirty hours, the water lost by evaporation being restored from time to time. The results in all three methods agreed well within the limits of experimental error.

0.2496 gram of material gave 0.1476 gram magnesium pyrophosphate, or 16.46 per cent. phosphorus.

0.1637 gram of material gave 0.0968 gram magnesium pyrophosphate, or 16.45 per cent. phosphorus.

0.1750 gram of material gave 0.1064 gram magnesium pyrophosphate, or 16.91 per cent. phosphorus.

REACTIONS AND COMPOSITION.

(1) It has been shown by analytical results that successive preparations do not possess the same composition.

(2) The products of its decomposition by water or acids are numerous. Phosphine, hydrogen, ammonia, sodium hypophosphite, sodium hydroxide, and red phosphorus have been detected and there is much reason to believe that salts of phosphorous and of phosphoric acids are also formed. There is no one salt of definite composition which can be conceived to be formed by these two reagents, *vis.*, sodamide and yellow phosphorus, capable of yielding all these products simultaneously in the proportions found.

(3) It has been shown that the instability of the compound in the presence of air, heat, and the common solvents is very great, while, on the other hand, the common organic solvents, alcohol excepted, are, if dry, without action upon any of its constituents. Owing to these facts the attempt to purify the compound or to isolate any of its constituents has met with no success.

(4) Sodamide may break down in the presence of substances capable of uniting with it in either one of two ways. Thus, as in the union with water, the point of rupture in the sodamide is between the sodium and the amido group. On the other hand, as Titherly¹ has shown, when sodamide reacts with many organic

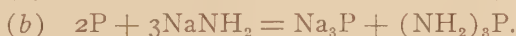
¹ *J. Chem. Soc. (London)*, 71, 460.

compounds, especially the organic amides, an amido hydrogen atom in sodamide is substituted by the organic residue.

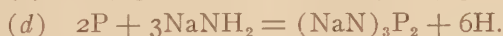
(5) The behavior of phosphorus is even more anomalous. The long list of phosphorus compounds, prepared by chemists from the time of Magnus and Rose to the present, show clearly that the distribution of the valencies of phosphorus toward groups with which it is capable of uniting lead to no certain generalizations. To a certain extent, but in a less degree, phosphorus resembles carbon in the ability to form complex chains. Vigier's compound has had ascribed to it the formula Na_3P , but it certainly contains an appreciable amount of Na_4P_2 , for its phosphine is very inflammable. In short, it is a question whether any such simple formula as has been given can stand for the composition of sodium phosphide and similar compounds.

In view of all these facts the reaction between phosphorus and sodamide in the presence of an inert gas may be supposed to take place in any of the following ways:

(1) Assuming sodamide to break down into sodium and amidogen,



(2) Assuming it to substitute phosphorus for hydrogen in the amide group,



Two methods were employed in the attempt to determine which of these reactions occur:

(1) Analysis of the products of decomposition.

(2) To conduct the synthesis of the compound in such a manner that the evolved gases may be collected and their nature and amount determined. The solution of the problem along these lines would be comparatively easy, if the material were not so complex in composition and so unstable.

In the prosecution of the first method, it was ascertained that the material contains sodium hypophosphite, formed through the action of excess of phosphorus upon sodium hydroxide, always found in sodamide in amounts varying from 1 to 10 per cent.

This is to be distinguished from the sodium hypophosphite formed by the decomposition of the material with water. The reaction for the former is:



In addition to the constant presence of small amounts of red phosphorus, already alluded to, the inability to exclude air and moisture completely also insures the presence of traces of other oxygen compounds of phosphorus.

The analysis to determine the products of decomposition was carried on in three ways:

(1) *Volumetrically*, as already described, whereby the proportion of phosphine and of hydrogen was determined.

(2) *Qualitatively*, to show the presence of sodium hydroxide and of the salts of the acids of phosphorus.

SIMULTANEOUS DETERMINATION (QUALITATIVE) OF HYPOPHOSPHOROUS, PHOSPHOROUS, AND PHOSPHORIC ACIDS.

As is well known, the recognition of hypophosphorous, phosphorous and phosphoric acids when all three are present in the same solution is a difficult matter. The presence of hypophosphorous acid could be assumed in view of the reaction between sodium hydroxide and phosphorus given above. The fresh solution also reduces potassium permanganate immediately, as do hypophosphites. The decomposition of sodium phosphide by water also yields sodium hypophosphite, as was proven by decomposing the sodium phosphide made after Vigier's method. But that phosphorous or phosphoric acids, or both, are also present is shown by the fact that, after neutralization of the sodium hydroxide by acetic acid, the addition of lead acetate solution gives a white precipitate, whereas lead hypophosphite is soluble in acetic acid. When ammonium molybdate is added to the solution obtained by decomposing the material with water, a blue coloration was observed which, on standing or gentle warming, became colorless, and with the addition of a few drops of nitric acid, well diluted, and gentle heat, the usual ammonium phosphomolybdate precipitate, indicative of phosphoric acid, was obtained.

AMMONIUM MOLYBDATE REDUCTION BY PHOSPHINE.

Knowing the energetic reducing properties of hypophosphorous acid, it was at first thought that the blue color, observed above, was due to reduction of the molybdic anhydride to the sesquioxide by the hypophosphorous acid, and that this could, therefore, advantageously be used as a qualitative test for the presence of hypophosphorous acid. But when the pure acid was prepared free from traces of phosphine no such reduction occurred. When it is recalled that phosphine is even more energetic as a reducing agent than hypophosphorous acid, and that phosphine is, to some extent, soluble in water and more so in a strong solution of sodium hydroxide, the reduction of the molybdic anhydride must be ascribed to the presence of phosphine. In confirmation of this observation it is known that phosphorous acid, reduced with nascent hydrogen, yields phosphine and hypophosphorous acid, and when ammonium molybdate solution is added to this reduction product of phosphorous acid the blue coloration is observed.

QUANTITATIVE DETERMINATION OF SODIUM PHOSPHIDE.

(3) *Quantitatively*, to determine how much of the phosphorus in the material went to the formation of phosphine, and how much to the formation of oxygen or other compounds of phosphorus when water was employed to decompose it. The material was decomposed by alcohol to prevent ignition of phosphine, the oxidation products of which would be dissolved in the liquid and vitiate the results. The solution was boiled to expel the phosphine, oxidized with nitric acid, and the phosphoric acid precipitated with magnesia mixture.

0.1418 gram of material gave 0.042 gram magnesium pyrophosphate, or 8.24 per cent. phosphorus.

As the total phosphorus obtained from the material averaged 16.61 per cent., it is seen that the result of this experiment indicates that half of the phosphorus of the compound disappeared as phosphine, and the other half remains in solution as a salt of one or more of the acids of phosphorus.

SYNTHETIC DETERMINATION OF NATURE OF INITIAL REACTION.

The synthesis of the compound was carried on by the aid of the

apparatus described under Fig. 2. In the bottom of the generator *A* was placed a small cup of sheet aluminum to prevent the apparatus from breaking in the sudden heat generated by the reaction. After filling the apparatus with dry carbon dioxide, about 0.4 gram of phosphorus dried by benzene and approximately 0.7 gram of powdered sodamide were dropped into the cup and carbon dioxide was again passed through for some time. No combination took place in the presence of this inert gas at ordinary temperatures. The Hempel burette, filled with sodium hydroxide solution, was attached after introducing into it a measured small portion of oxygen to act as a gas cushion. On gentle heating under diminished pressure, a quantity of gas was forced over, most of which was absorbable. After the generator had cooled to the normal temperature, dry benzene (which does not decompose the material) was admitted through the funnel and all the gas driven into the burette.

Deducting for the oxygen, there was a remainder of 7.58 cc. This gas was transferred to a eudiometer, exploded over mercury with a known excess of oxygen, the oxygen remaining absorbed by potassium pyrogallate solution and the remainder calculated as nitrogen. The results, which, of course, are merely approximate, show that both nitrogen and hydrogen are liberated in the reaction, the latter gas being in slight excess. Since ammonia is also liberated, the two equations which best accord with those conditions are (a) and (c), page 39.

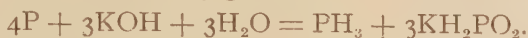
Thermometric measurements of the temperature at which combination takes place between these two reagents are of little value. The reaction began at 150° and in a few seconds rose to nearly 250°.

THEORETICAL CONSIDERATION OF SOURCE OF HYDROGEN.

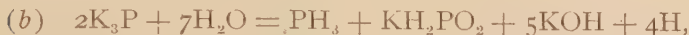
The invariable presence of hydrogen among the gases formed when the material is decomposed by water, and also in the formation of phosphine by other methods, calls for some consideration. In regard to the formation of this gas, no information could be obtained from the published work of those who had investigated the compounds of phosphorus and hydrogen.

For the formation of phosphine in the usual way from phos-

phorus and potassium or sodium hydroxide, heated together; the following equation is usually given:



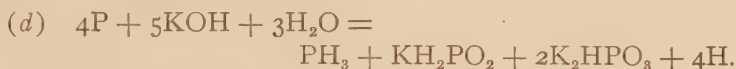
Without doubt the reaction is far more complicated, and for the sake of clearness may be assumed to take place in the following stages:



(c) with excess of alkali, as is always the case,

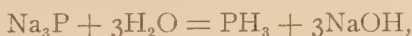


whence by combination of these three and reduction to simplest terms there remains the completed equation:

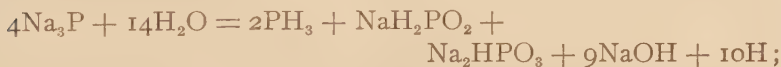


That (*d*) more nearly represents the actual reaction is evidenced by the fact that both of these acids of phosphorus can be shown to be present in the solution from which the phosphine has been distilled. It is not claimed that the equation represents the actual proportion of the products; it shows merely what has not been shown, that hydrogen and at least two of the acids of phosphorus are formed when phosphine is generated in the usual way.

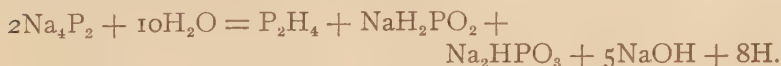
In a similar way we might expect a compound of the formula Na_3P to unite with water, thus:



but in this case also analysis reveals more complex changes, probably represented by



and to account for the inflammable phosphine, traces of the sodium salt of which are undoubtedly present,



SIGNIFICANCE OF AMMONIA-NITROGEN IN THE COMPOUND.

Reference should be made here to the occurrence of ammonia-nitrogen in the material. Analysis yields 22.64 per cent. NH_3 ,

equivalent to 21.3 per cent. NH_2 . That this is not present as unchanged sodamide is definitely known from:

(1) The appearance of the product of the reaction before pulverizing it, for its uniform dark brown color serves to distinguish it from intermingled sodamide. In no case, except in Portion I, was free sodamide visible.

(2) This amount of NH_2 would demand over 51 per cent. of the compound to be sodamide, of which 30.58 per cent. would be sodium. The absence of free nitrogen from the gases obtained by decomposition is, of itself, proof of the absence of unchanged sodamide. But further, if, as has been shown by analyses, the amount of phosphorus in phosphine represents one-half of the phosphorus present in the material as sodium phosphide, there would, on this basis, be 19.29 per cent. sodium phosphide. Of this, 13.32 per cent. would be sodium, and thus to assume sodamide present in sufficient amount to account for all of the ammonia would require for the phosphide and amide of sodium all of the sodium and all of the nitrogen, but leaving 13.7 per cent. of the phosphorus unprovided for. It is justifiable, therefore, to assume some substituted amide of phosphorus analogous to the substituted amides described by Titherly to be present in the material along with the sodium phosphide, hypophosphite, etc. It could hardly be surmised that any ammonium compounds would be formed under these circumstances. In the presence of other constituents of this material it is impossible to say how such compounds would break down, but it is very probable they would add to the instability of the material.

SODAMIDE AS A REAGENT.

Sodamide lends itself very readily to synthetical operations, and yet the chief drawback to its use is the difficulty of keeping it in the pure condition. Its use is also further hampered by the difficulty of separating the by-products from the end-products desired. This is well illustrated by the present work. Sodamide affords a quick method for the preparation of impure sodium phosphide and a number of its by-products have led into interesting theoretical discussions. Much work remains to be done with sodamide in the field of inorganic chemistry. While

in the present instance the reaction is not a clean-cut one, it would be unfair to assume that with elements not so closely related, according to our present views of the periodic system, as are phosphorus and nitrogen, results of a far more satisfactory character will not be gained.

FINAL SUMMARY.

I. Sodamide.—

(1) Yields hydrogen and nitrogen in varying amounts when decomposed by water.

(2) Hydrogen can be almost completely eliminated

(a) By prolonged heating at high temperatures with excess of NH_3 .

(b) By long standing in closed bottles.

(3) Nitrogen is always present and is very probably due to sodium triazoate or some analogous compound, the formation of which in sodamide is due to partial oxidation of ammonia, as pointed out

(a) In process of manufacture of sodamide.

(b) By long standing in presence of dry air.

(4) Occurrence of nitrous and hyponitrous acids in sodamide that has become yellow through exposure to dry air.

(5) Formation of disodium cyanamide in the wet way.

II. Sodamide and Phosphorus Pentachloride.—

(1) Formation of a compound which cannot be isolated from the associated by-products without undergoing change.

(2) When thus separated by nitric or acetic acids an inert substance is obtained which corresponds to the formula PO_2N , or to PONHOH .

III. Sodamide and Yellow Phosphorus.—

(1) Forms a complex mixture of sodium phosphide, hypophosphite, and presumably also an amide of phosphorus, etc.

(2) Discussion of various methods devised for the quantitative decomposition of explosive and easily volatile substances.

(3) Elaboration of methods for simultaneous recognition of hypophosphorous, phosphorous and phosphoric acids.

(4) Discussion of the source of hydrogen in the preparation of phosphine.

(5) Qualitative test for phosphine by ammonium molybdate.

BIOGRAPHY.

William Phillips Winter was born at Galion, Ohio, February 17, 1866. His course of instruction in the Public and High schools was followed by two years of College preparatory training at Oberlin (Ohio) College. He then entered Ohio Wesleyan University, at Delaware, Ohio, from which he was graduated in the Classical course in 1887. He received the degree of Master of Arts from the same Institution three years later. The greater part of his time since graduation has been spent in College teaching.

In 1895-6 he attended Johns Hopkins University as a special student in Biology, Geology and Mineralogy. In the Summer of 1900 he pursued the study of Chemistry at Cornell University. He entered Johns Hopkins University for the purpose of studying Chemistry, in October, 1901. In the following year he was awarded a University Scholarship, and during the present year he has been filling the position of Lecture Assistant to Professor Renouf in the Minor course.

His subordinate subjects have been Physical Chemistry and Zoology.

